Proton Exchange Membranes Prepared by Simultaneous Radiation Grafting of Styrene onto Poly(tetrafluoroethylene-*co*-hexafluoropropylene) Films. II. Properties of Sulfonated Membranes

MOHAMED MAHMOUD NASEF, HAMDANI SAIDI, HUSSIN MOHD NOR, OOI MUN FOO

Membrane Research Unit, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, Jalan Semarak, 54100 Kuala Lumpur, Malaysia

Received 23 September 1999; accepted 7 February 2000

ABSTRACT: Proton exchange membranes were prepared by radiation-induced grafting of styrene onto commercial poly(tetrafluoroethylene-*co*-hexafluoropropylene) films using a simultaneous irradiation technique followed by a sulfonation reaction. The resulting membranes were characterized by measuring their physicochemical properties such as water uptake, ion exchange capacity, hydration number, and proton conductivity as a function of the degree of grafting. The thermal properties (melting and glass transition temperatures) and thermal stability of the membrane were also investigated using differential scanning calorimetry and thermal gravimetric analysis, respectively. Membranes having degrees of grafting of 16% and above showed proton conductivity of the magnitude of 10^{-2} Ω^{-1} cm^{-1} at room temperature, as well as thermal stability at up to 290°C under an oxygen atmosphere. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2443–2453, 2000

Key words: proton exchange membrane; radiation grafting; styrene; poly(tetrafluoroethylene-*co*-hexafluoropropylene); sulfonation

INTRODUCTION

Ion exchange membranes bearing sulfonic acid groups were proposed for use in various electrochemical cells such as water electrolyzers and proton exchange membrane (PEM) fuel cells,[1] because of the complete dissociation of sulfonic acid groups, which leads to high ionic conductivity and low ohmic losses at high current density.[2,3] There is currently a high demand to develop new membranes with a combination of high conductivity, stability, and low cost to enhance the practical use of PEM fuel cells because the commercially available perfluorinated membranes are excessively expensive.[4,5]

Several new fluorinated membranes such as Nafion®/Gortex composite,[6] Gore-Select™ (Gore Co.), and a polytrifluorostyrene-based BAM membrane[7] (Ballarad Advanced Materials) were developed recently and showed good performance in a PEM fuel cell. Moreover, a few nonfluorinated membranes such as the polyether ether ketone (PEEK)-based *Aventis*[8] (Hoechst) and the styrene-ethylene/butylene-styrene triblock copolymer[9] *Dias 585* (Dias Co.) were also developed and tested in fuel cells.

In the development of new membranes, modification of preexisting polymer films by radiation-induced grafting of a chemical functionality is an

Correspondence to: M. M. Nasef (mhamoudeithar@mailcity.com).

Contract grant sponsor: Malaysian Ministry of Science, Technology, and the Environment.

Journal of Applied Polymer Science, Vol. 78, 2443–2453 (2000)

advantageous technique, particularly in terms of shaping and controlling the composition and properties of the membrane.[10,11] Experimental radiation grafted sulfonic acid membranes based on commercial poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) films were developed by Büchi and coworkers and were found to be stable for 1400 h in a PEM fuel cell at temperatures up to 80°C.[12–14] The possibility of using commercial radiation grafted sulfonic acid membranes as polymer electrolytes in PEM fuel cells was explored by Guzman-Garcia et al.[15] These membranes were very recently tested in a PEM fuel cell and demonstrated satisfying performance with an initial stability up to 1000 h.[16] Furthermore, a number of studies reported the preparation of various proton exchange membranes by radiation-induced grafting of styrene onto other fluorinated polymers and subsequent sulfonation.[17–23] Because of the chemical stability needed, the base polymers were confined to fluorinated polymers. Among fluorinated polymers, FEP is well known for its high radiation resistance. Therefore, the use of such film as a polymer substrate provides a possibility for using a wide range of doses and dose rates.

Roully et al.[24] reported the preparation of proton exchange membranes by grafting of styrene onto FEP film using a simultaneous irradiation technique followed by sulfonation. However, in their work the effect of grafting conditions on the degree of grafting was not disclosed and only a thin 50-μm FEP film was used as the polymer matrix. In the first part of this study styrene was grafted onto a thicker 120-μm FEP film using a simultaneous irradiation technique under different conditions.[25] The effect of the grafting conditions on the degree of grafting was kinetically studied and the mechanical and structural changes taking place in the graft copolymers were evaluated. The grafting conditions showed a strong effect on the degree of grafting of the obtained FEP-*g*-polystyrene films.

In the present study the grafted FEP (FEP-*g*-polystyrene) films were sulfonated and the physicochemical properties of the obtained FEP-*g*-polystyrene sulfonic acid membranes investigated in correlation with the degree of grafting. The thermal properties of the membranes such as the melting temperature (T_m) and glass-transition temperature (T_g), as well as thermal stability, were also investigated. The original FEP and FEP-*g*-polystyrene films were included as references.

EXPERIMENTAL

Materials and Grafting Procedure

The FEP-*g*-polystyrene films were prepared by radiation-induced grafting of styrene (Fluka 85960, >99%) onto a FEP film (Porghof) with a thickness of 120 μm using a simultaneous irradiation technique. A glass ampoule containing a FEP film of known weight was immersed in the styrene monomer with concentrations in the range of 20–60 vol % and diluted with dichloromethane (J. T. Baker, reagent grade). The ampoule was irradiated using γ rays from a Co-60 source (Malaysian Institute for Nuclear Technology Research) to a total dose of 20 kGy at a dose rate of 0.37 Gy/s under a nitrogen atmosphere at room temperature. The grafted films were washed thoroughly with toluene and soaked therein for 16 h, then dried under a vacuum until constant weight. More details on the grafting conditions and properties of the obtained grafted FEP films can be found elsewhere.[25] The degree of grafting was calculated using the following equation:

$$\text{degree of grafting } (\%) = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

where W_g and W_0 are the weights of the grafted and original FEP films, respectively.

Sulfonation

The grafted FEP films were sulfonated using a sulfonation mixture composed of 30 parts chlorosulfonic acid (Fluka) in 70 parts of 1,1,2,2-tetrachloroethane (Fluka) (v/v). The grafted films were first washed with dichloromethane, soaked therein for 30 min, removed, and dried in a vacuum oven for 1 h. The dried films were placed in a glass reactor containing the sulfonation mixture, and the temperature was maintained at 90°C using an oil bath. The sulfonation reaction was allowed to continue for 4 h under an N_2 atmosphere. After completion of the reaction, the sulfonated membranes were removed and washed several times with 1,1,2,2-tetrachloroethane and dichloromethane to remove the excess chlorosulfonic acid. The sulfonated membranes were then hydrolyzed with 0.5*M* KOH solution and regenerated by boiling with 1*M* HCl. The membranes were then washed several times with deionized water to ensure the complete removal of the acid.

Finally, the membranes were stored in the dark under water.

Water Uptake

Water uptake measurements were carried out by equilibrating clean and vacuum dried (1 torr, 80°C, 24 h) membrane samples in acid form in deionized water (18 MΩ cm) for 4 h. The swollen membrane samples were removed, the excess of water adhering to the surface was quickly blotted by absorbent paper, and then the samples were weighed. The dry weight of the samples referred to the salt (K^+) form of the membrane. The water uptake of the swollen membrane was determined as reported by Roully et al.[24] using eq. (2):

$$\text{water uptake (wt \%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (2)$$

where W_w is the weight of the swollen membrane in the acid form and W_d is the weight of the dried membrane in the K^+ form. All the obtained values were corrected for the salt form.

Ion Exchange Capacity (IEC)

The membrane samples (2×2 cm^2) in acid form were immersed into 50 mL of 0.5*M* KCl for 16 h at room temperature. The protons (H^+) released in the solution were titrated with standardized 0.5*M* KOH solution by an automatic titrator (Metrohom, Switzerland) until pH 7 was reached. Membrane samples were regenerated into acid form by boiling with 3.5*M* HCl for 3 h. From the volume of KOH consumed in titration, the IEC of the dry membrane per unit mass (meq/g) and per unit volume (meq/mL) were calculated by taking the membrane dimensional changes during swelling into account. The theoretical IEC was calculated based on the presence of full (100%) sulfonation in all membranes at various degrees of grafting and was used as a reference.

The dimensional changes of the wet membranes were determined and compared with the corresponding values of the dry ones. A thickness gauge (Mitotuyo, Japan) with a resolution of 0.005 mm was used to measure the membrane thickness. The length and width of the membrane samples were determined by measuring the distance between two glass slides placed on the edges of the membrane using a digital sliding caliper (Mitotuyo) with a resolution of 0.01 mm.

The degree of sulfonation was calculated from the volume of KOH consumed and the total number of styrene units obtained from the degree of grafting as reported by Roully et al.[24] The equivalent weight (EW) was calculated from eq. (3):

$$\text{EW} = W_d/V_{\text{KOH}} \times 0.05 \quad (3)$$

where W_d is the weight of the dry membrane and V_{KOH} is the volume of KOH consumed in titration.

Proton Conductivity

The proton conductivity of the membranes was measured at room temperature by AC impedance spectroscopy. Measurements were carried out on membranes in the acid form using a frequency response analyzer (Solartron, 1250) in combination with an electrochemical interface (EG&G Princeton Applied Research) at a 0.01–100 kHz frequency range. The circular shaped swollen membrane samples were clamped between two blocked stainless steel electrodes located in a conductivity cell. Fresh electrodes were used for each experiment to maintain electrode sensitivity. The resistance was obtained from the intercept of the impedance curve with the real axis at the high frequency end. The resistance values were corrected by deduction of the resistance of the conductivity cell without samples. The proton conductivity was calculated from the resistance after taking the surface area and the thickness of the membrane samples into account.

Differential Scanning Calorimetry (DSC)

The DSC measurements were carried out using a Pyris-1 calorimeter (Perkin Elmer). The membrane samples were dried at 80°C in a vacuum oven (10^{-4} torr) for 7 days prior to the DSC runs. Original FEP and grafted FEP films were used as references. Typical samples weighed 5–10 mg. All DSC runs were made in a temperature range of 50–400°C at a constant heating rate of 20°C/min under a nitrogen atmosphere. The T_g and T_m were obtained from the thermograms by means of Pyris-1 commercial software.

Thermal Gravimetric Analysis (TGA)

The TGA measurements were performed using a Perkin–Elmer TGA-7. Thermograms were obtained for samples of vacuum dried membrane, original, and grafted FEP films having typical

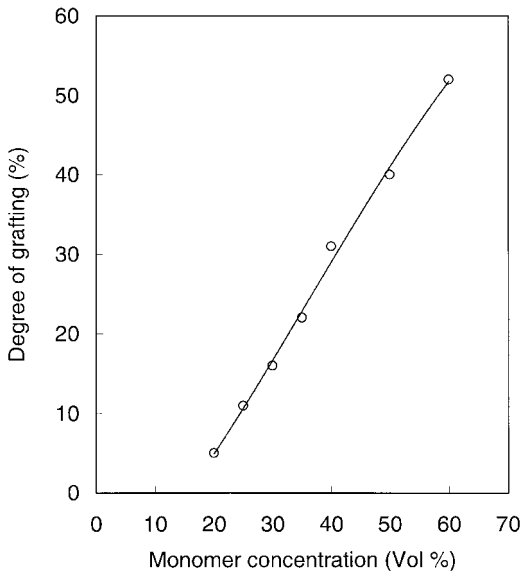

Figure 1 The relationship between the degree of grafting and the monomer concentration for grafting of styrene onto FEP films. Grafting conditions: 20 kGy dose, 1.3 kGy/h dose rate, dichloromethane diluent, 120-μm film thickness, 30°C and N_2 atmosphere.

weights of 10–20 mg in a temperature range of 50–700°C. All TGA runs were made at a constant heating rate of 20°C/m in a nitrogen atmosphere.

Commercial Nafion 117 (Du Pont) membranes were used as a reference. They were converted to proton form by boiling in HNO_3 (33%) for 2 h and then washed free of acid with several changes of deionized boiling water.

RESULTS AND DISCUSSION

Grafting of styrene onto FEP films by the simultaneous irradiation technique resulted in grafted films having various degrees of grafting (5–52%). The degree of grafting in the membranes was found to increase with the increase in the monomer concentration as depicted in Figure 1, which shows the relationship between the degree of grafting and the monomer concentration. This behavior was attributed to the increase in the styrene diffusion and its concentration inside the grafting layers, despite the fact that the FEP film hardly swells in common monomers and solvents. The reason behind such behavior is the proceeding of the grafting reaction by the front mechanism. Based on this mechanism, styrene grafting onto FEP film was suggested to be started at layers close to the film surface and it moves internally towards the middle of the film by progressive diffusion through successive swollen grafted layers.[25] These results are in complete agreement with those reported for grafting styrene onto FEP films using the preirradiation technique.[26]

Sulfonation of the grafted FEP films with various degrees of grafting results in FEP-*g*-polystyrene sulfonic acid membranes having various equivalent weights. Figure 2 shows a generalized molecular structure of the FEP-*g*-polystyrene sulfonic acid membrane. The degree of sulfonation for all the membranes was found to be in the range of 94–100% i.e., the ratio of the sulfonic acid groups to the phenyl groups of polystyrene can be assumed to be equal to 1. Therefore, all the membrane properties are discussed only in correlation with the degree of grafting in this study.

Water Uptake

The relationship between the membrane water uptake and the degree of grafting of FEP-*g*-polystyrene sulfonic acid membranes is shown in Figure 3. The water uptake was found to increase gradually and linearly with the increase in the degree of grafting. It is well known that the water uptake of the membranes is related to the degree of grafting and subsequently the amount of sulfonic acid groups available. Therefore, the results obtained here can be attributed to the increase in the hydrophilicity imparted to the membranes by the incorporation of sulfonic acid groups with the increase of the degree of grafting. In addition, the increase in the content of sulfonated polystyrene side chain grafts leads to a decrease in the fluorinated domain (FEP) in the membranes; as a result, the hydrophobicity of the membrane decreases. The water uptake of the reference Nafion 117 was found to be around 39%.

Ion Exchange Capacity

Figure 4 shows the relationship between the IEC and the degree of grafting of FEP-*g*-polystyrene

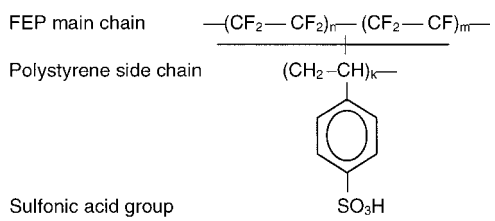

Figure 2 A generalized molecular structure of the FEP-*g*-polystyrene sulfonic acid membrane.

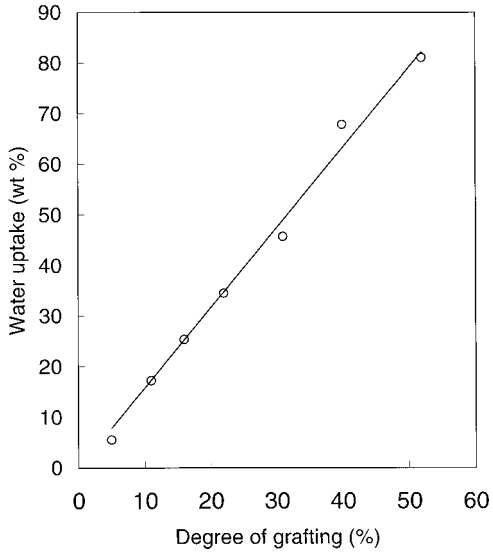

Figure 3 The relationship between the membrane water uptake and the degree of grafting of FEP-*g*-polystyrene sulfonic acid membranes.

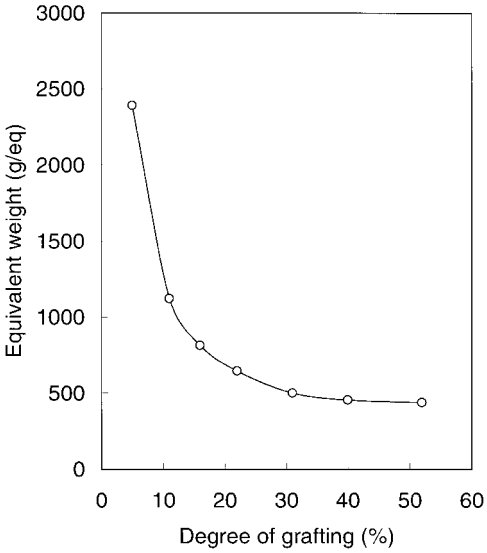

Figure 5 The relationship between the equivalent weight and the degree of grafting of FEP-*g*-polystyrene sulfonic acid membranes.

sulfonic acid membranes. Observe that the IEC increases as the degree of grafting increases. The increase in the degree of grafting from 5 to 52% leads to an increase in the IEC from 0.4 to 2.3 per unit mass (meq/g) and from 0.7 to 3.6 per unit volume (meq/mL) of the dry membrane. The corresponding IEC values of the Nafion 117 membrane are equal to 0.9 meq/g and 1.9 meq/mL. As the degree of grafting increases, the content of the polystyrene grafts in the polymer matrix increases and, as a result, more benzene rings are available to host sulfonic acid groups. Therefore, a desirable number of ionic sites can be achieved by controlling the degree of grafting. These results are in a complete agreement with those reported in the literature for similar FEP-based membranes that were not as thick (50 μm). The IEC of those membranes was found to increase from 0.7 to 2.5 meq/g and from 1.9 to 3.9 meq/mL with the increase in the degree of grafting from 13 to 52%.[24] Moreover, these results are in harmony with those reported for other proton exchange membranes based on poly(tetrafluoroethylene),[17] poly(vinylidene fluoride) (PVDF),[19,20] and poly(tetrafluoroethylene-*co*-perfluorovinylether) (PFA).[22,23]

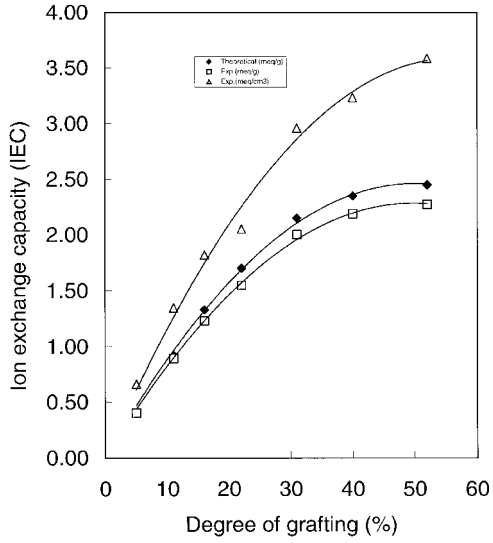

Figure 4 The relationship between the ion exchange capacity and the degree of grafting of FEP-*g*-polystyrene sulfonic acid membranes. (◆) Theoretical (meq/g), (□) experimental (meq/g), and (△) experimental (meq/mL) values.

It can also be seen that the experimental results of the IEC on a weight basis are slightly lower than those of the IEC theoretical values that were estimated based on 100% sulfonation. This is most probably due to the presence of a few unsulfonated phenyl groups and/or the presence of sulfonic acid groups in sites that are not accessible to water and diffusing protons as suggested by Hietala et al.[27]

Figure 5 shows the relationship between the equivalent weight and the degree of grafting of FEP-*g*-polystyrene sulfonic acid membranes. The

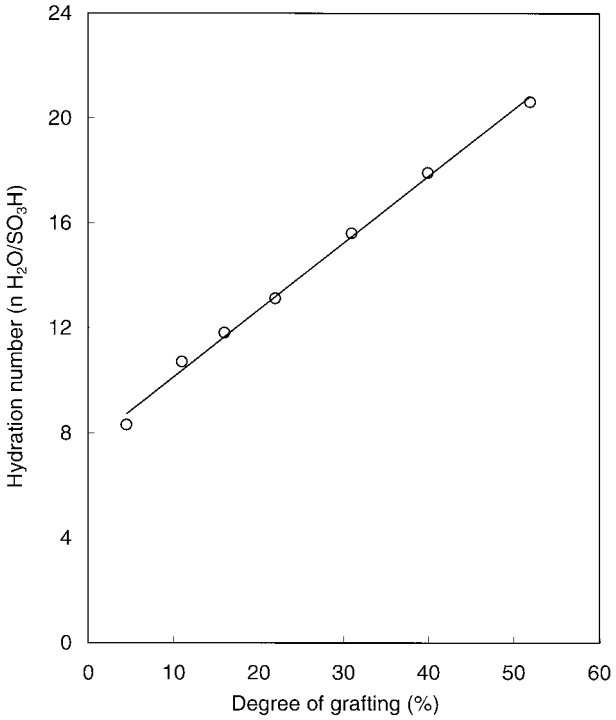

Figure 6 The relationship between the hydration number (nH_2O/SO_3H) and the degree of grafting of FEP-*g*-polystyrene sulfonic acid membranes.

equivalent weight was found to decrease with the increase in the degree of grafting. The equivalent weight decreased from 2389 to 439 g/eq with the increase in the degree of grafting from 5 to 52%. This can be understood based on the fact that the degree of grafting determines the amount of ionic sites incorporated in the membrane. Accordingly, the amount of polystyrene incorporated into the FEP backbone determines the number of sulfonic acid sites. Therefore, sulfonation of a membrane having a high degree of grafting results in a low equivalent weight and the opposite is true. These results suggest that desirable equivalent weights can be obtained by the variation of the degree of grafting. Similar results were reported for FEP-based sulfonic acid membranes prepared by preir-radiation.[14] The Nafion 117 membrane used as a reference was found to have an equivalent weight of 1115 g/eq.

Hydration Number

The relationship between the hydration number of the sulfonic acid groups and the degree of grafting of FEP-*g*-polystyrene sulfonic acid membranes is shown Figure 6. The hydration number (nH_2O/SO_3H) was found to increase linearly with the increase in the degree of grafting. The increase in the degree of grafting from 5 to 52% led to an increase from 8 to 21 in the average number of water molecules per sulfonic acid group. These results are lower than those reported for thinner FEP-based membranes, which showed an increase in the hydration number in a range of 12–27 with the increase in the degree of grafting from 13 to 52%.[24] The difference between both results can be ascribed to the difference in the applied grafting conditions, which cause a difference in the structural changes that were built up in the membranes. This behavior was explained on the basis of a cumulative effect of three main factors: the increase in the sulfonic acid groups, the increase in the hydrophilicity, and the decrease in the degree of crystallinity of the membrane with the increase in the degree of grafting.[28] The number of water molecules per sulfonic acid group in the Nafion 117 was found to be around 23. This result is in good agreement with that reported by Zawodzinski et al.[29] and Halim et al.[30]

Proton Conductivity

Figure 7 shows the relationship between proton conductivity and the degree of grafting of FEP-*g*-

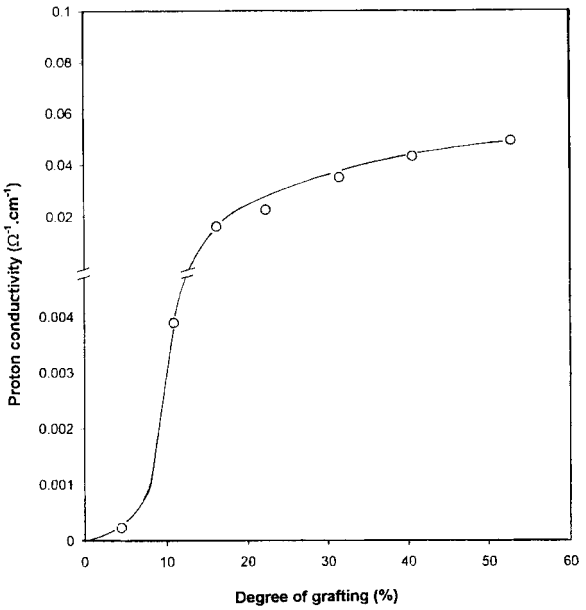

Figure 7 The relationship between the proton conductivity and the degree of grafting of FEP-*g*-polystyrene sulfonic acid membranes at room temperature.

polystyrene sulfonic acid membranes at room temperature. The results show that the proton conductivity increases sharply with the increase in the degree of grafting at the beginning and tends to level off beyond a degree of grafting of about 16%. The sharp increase in the conductivity at the beginning is most likely attributable to the cumulative effect of the increase in the amount of sulfonic acid groups, the increase in the water uptake, and the increase in the hydration number of sulfonic acid with the increase in the degree of grafting. The tendency of the proton conductivity to level off beyond a 16% degree of grafting can be explained by taking the location of the sulfonated polystyrene grafts into consideration. At low degrees of grafting, the polystyrene grafts are located near the surface of the film while its middle remains ungrafted and subsequently it exerts high local resistance to proton transport, resulting in low proton conductivity. As the degree of grafting approaches a value of 16% more grafts are distributed near the middle part of the membranes, resulting in diminution of the local resistance; consequently, the proton conductivity increases. A further increase in the degree of grafting does not bring considerable changes to the proton conductivity because of the possible achievement of a homogenous distribution of the sulfonated polystyrene grafts in the membrane. These results show a trend similar to that of the FEP-based 50-μm thickness membrane, despite their lower values.[13,24] The corresponding proton conductivity of Nafion 117 was found to be equal to 5.3×10^{-2} Ω^{-1} cm^{-1} at room temperature. This value is in good agreement with that reported by Zawodzinski et al.[31] and Rieke and Vanderborgh.[32]

Thermal Properties

Figure 8 shows the DSC thermograms of the original FEP film, the FEP-*g*-polystyrene film having a 40% degree of grafting, and the FEP-*g*-polystyrene sulfonic acid membrane having a 40% degree of grafting. The original FEP film has two transitions representing T_g and T_m at 116.4 and 267.9°C, respectively [Fig. 8(A)]. The grafted FEP film shows a T_g at 119.3°C and a T_m at 266.2°C [Fig. 8(B)]. The grafted and sulfonated membrane with a degree of grafting of 40% have a T_g and T_m at 120.9 and 264.2°C, respectively [Fig. 8(C)]. It can be clearly observed that grafting of styrene onto the FEP film caused an increase in the T_g in combination with a slight decrease in the T_m. Similarly, sulfonation of grafted FEP films led to a further increase in the T_g and decrease in the T_m. These results can be explained by taking into account the nature of the incorporated polystyrene grafts and the location at which the grafting takes place.

The incorporation of polystyrene side chain grafts, which are amorphous in nature, increases the amorphous fraction and restricts the mobility of the molecular chains of the FEP domain. Because the T_g is confined to the amorphous fraction in the film, it shifts to higher values. Moreover, the incorporation of sulfonic acid groups in the polystyrene side chains leads to ionic interactions, which most likely are in the form of physical crosslinking within the ionic domain. Consequently, the mobility of the molecular chains in the polystyrene domain is hindered and as a result the T_g is further increased.

The slight decrease occurring in the T_m upon the introduction of polystyrene side chain grafts shows that the original crystal size distribution is slightly affected by styrene grafting and very little disruption in the crystalline region took place. These results suggest that polystyrene side chain grafts were mainly introduced into the entire noncrystalline (amorphous) region of the FEP matrix. The decrease in the T_m of the sulfonated membranes can be attributed to the deterioration occurring in the crystallites under the influence of the sulfonation of polystyrene grafts. This results in a strong interaction between the hydrophilic sulfonic acid groups and the hydrophobic FEP matrix, which leads to a partial crystal disruption. Similar results were discussed by Gupta et al.[33] and Hietal et al.[34] for styrene grafted and sulfonated FEP and PVDF membranes, respectively. These results indicate that the crystal disruption during the membrane preparation originates mainly after sulfonation. A T_m of 266.2°C was reported for a thinner FEP-*g*-polystyrene sulfonic acid membrane having the same degree of grafting.[33] The difference in the T_m between the two membranes is attributed to the difference in the preparation and drying conditions.

Thermal Stability

TGA thermograms of the original FEP and FEP-*g*-polystyrene films with a 40% degree of grafting and the FEP-*g*-polystyrene sulfonic acid membrane with a 40% degree of grafting are shown in Figure 9. The reason behind testing the membrane 40% degree of grafting was to have a fair

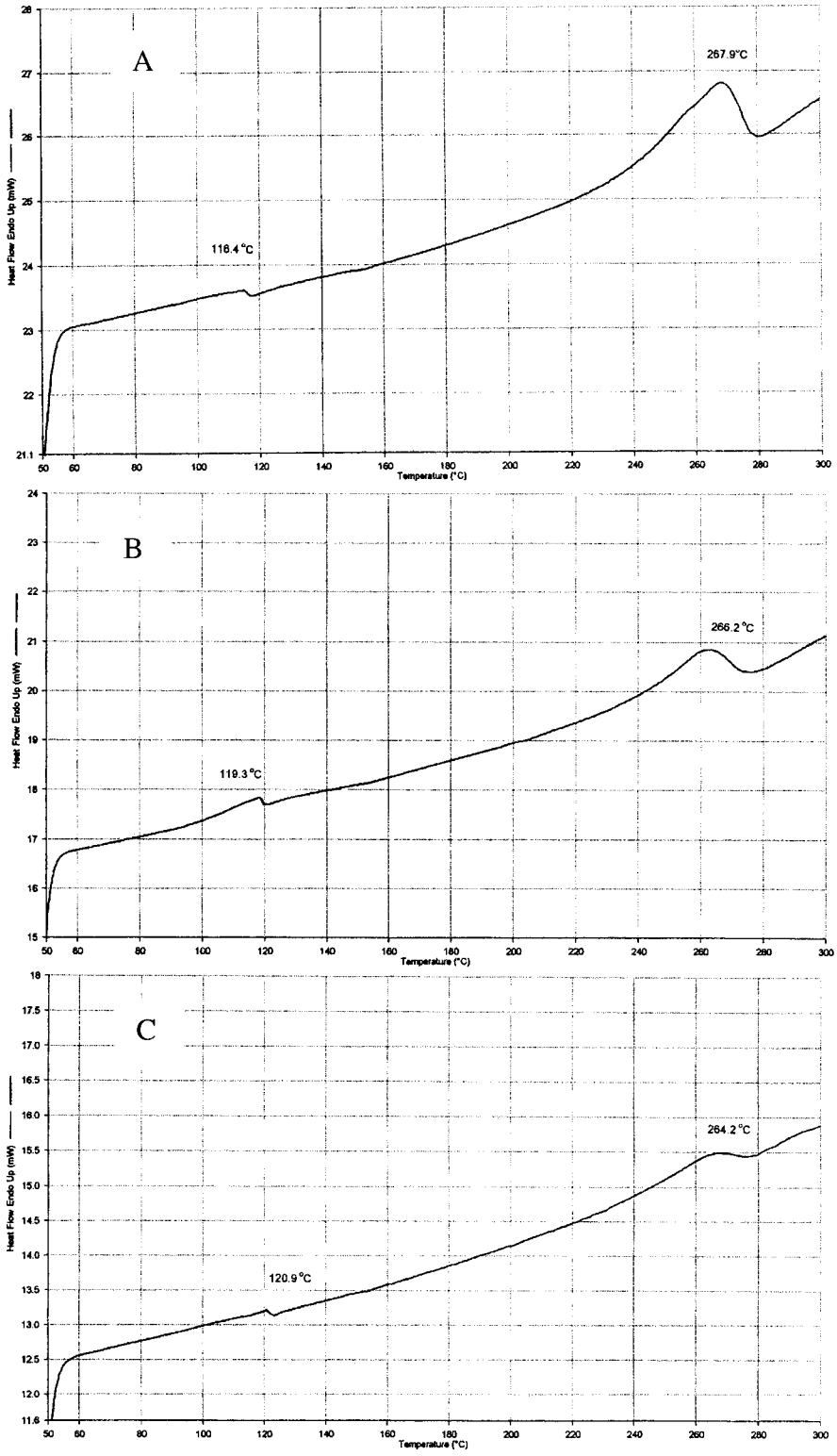

Figure 8 DSC thermograms of (A) the original FEP film, (B) the FEP-*g*-polystyrene film having a 40% degree of grafting, and (C) the FEP-*g*-polystyrene sulfonic acid membrane having a 40% degree of grafting.

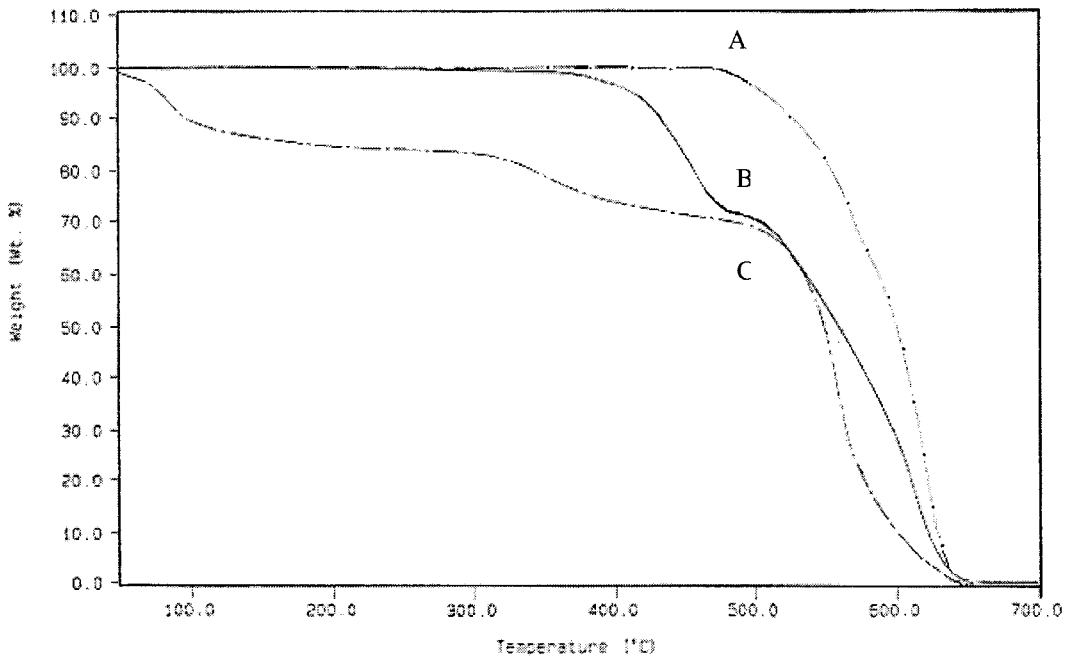

Figure 9 TGA thermograms of (A) the original FEP film having a 40% degree of grafting, (B) the FEP-*g*-polystyrene film having a 40% degree of grafting, and (C) the FEP-*g*-polystyrene sulfonic acid membrane having a 40% degree of grafting.

comparison with a thinner FEP-based membrane with the same degree of grafting and thermally treated under a nitrogen atmosphere.[35] The original FEP film shows thermal stability up to around 480°C, followed by a one-step degradation pattern as depicted in thermogram A in Figure 9. The incorporation of polystyrene grafts in the FEP matrix introduces a two-step degradation pattern where both of the grafted film components (polystyrene grafts and FEP main chain) show distinct degradation temperatures as depicted in thermogram B (Fig. 9). The polystyrene grafts start to degrade at about 370°C and continue until 460°C, followed by the degradation of the FEP matrix at around 480°C. This observation indicates the presence of two separated microdomains resulting from the incompatibility between the polystyrene grafts (hydrocarbon structure) and the FEP matrix (fluorocarbon structure) in the grafted film. It seems that the presence of polystyrene grafts does not change the decomposition temperature of the FEP matrix. Similar results were discussed by Gupta and Scherer[35] and Hietala et al.[36] upon studying the thermal analysis of styrene grafted FEP and PVDF films, respectively, under a nitrogen atmosphere. The sulfonation of the grafted films introduces a three-step degradation pattern as shown in thermogram C (Fig. 9). The weight loss represents the first step that starts below 100°C and continues to around 200°C. This is followed by a second degradation step, which continues to around 290°C. Finally, a third degradation step emerges when the film begins to decompose at 480°C. The initial weight loss in the sulfonated membrane, which can be seen in thermogram C (Fig. 9), is due to the loss of water bound to the membrane. The introduction of hydrophilic sulfonic acid groups imparts the hygroscopic nature that allows the membranes to absorb water. Part of this water is strongly bound to the sulfonic acid groups via hydrogen bonding and remains in the membrane even after raising the temperature above 100°C. Similar behavior was shown in radiation grafted and sulfonated FEP,[35] PVDF,[36] and PFA[37] based proton exchange membranes. Nafion 117 was also found to behave in the same manner.[38]

The massive weight loss in the second step (~290°C) is attributed to the elimination of sulfonic acid groups (desulfonation) while the weight loss at 480°C is due to the degradation of the FEP matrix. It can be observed that there is difficulty in getting a clear discrimination between desulfonation and decomposition of polystyrene grafts. Instead, the thermogram shows a continuous loss in the range of 300–460°C. Such observations

suggest that the sulfonation of polystyrene grafted FEP film makes the membrane more susceptible to thermal degradation and enhances its degradation compared to nonsulfonated ones. However, from these thermograms it may be stated that the membranes are thermally stable up to 290°C under the present experimental conditions. From the previous results it can be concluded that the trend of the thermal degradation of a FEP-*g*-polystyrene sulfonic acid membrane under an oxygen atmosphere is quite similar to that under a nitrogen atmosphere, which was reported in the literature.[35] However, under an oxygen atmosphere the degradation of the membrane components was found to start at lower temperatures. Moreover, the membrane completely vanished without leaving any residue under an oxygen atmosphere unlike the heat treatment under a nitrogen atmosphere, which left a residue of more than 20% of its original weight. This was most probably due to the complete conversion of the membrane residue, which was in a carbon form (ash) to the evolving CO_2. Details of the thermal stability investigations and thermal degradation behavior of FEP-*g*-polystyrene sulfonic acid membranes will be published in the future.[39] Nafion 117 membrane was found to be thermally stable up to 290°C in oxygen. This result is in a good agreement with the reported Nafion thermal stability in air.[40]

Thanks are due to Dr. Khairul Zaman and Dr. Kamaruddin Hashim for their assistance during the access of the cobalt-60 facilities at the Malaysian Institute for Nuclear Technology Research. Dr. Nasef wishes to gratefully acknowledge a fellowship given by the Universiti Teknologi Malaysia under a project for fuel cell development.

REFERENCES

1. Grubb, W. T. U.S. Pat. 2,913,511, 1959.
2. Yeo, R. S. in Perfluoronated Ionomer Membranes. ACS Symposium Series 180; Eisenberg, A., Yeager, H. L., Eds.; American Chemical Society: Washington, D.C., 1982.
3. Scherer, G. G.; Killer, E.; Grman D. Int J Hydrogen Energy 1990, 17, 115.
4. Ostroviski, D. I.; Torell, L. M.; Paronen, M.; Hietala, S.; Sundholm, F. Solid State Ionics 1997, 97, 315.
5. Lehtinen, T.; Sundholm, G.; Holmberg, S.; Sundholm, F.; Björnbom, P.; Bursell, M. Electrochim Acta 1998, 43, 1881.
6. Kolde, J. A.; Baher, B.; Wilson, M. S.; Zawodzinski, T.; Gottesfeld, S. In Proton Conducting Membranes for Fuel Cells I, PV 95-23, The Electrochemical Society Proceedings Series; Gottesfeld, S., Halpert, G., Landgrebe, A., Eds.; Electrochemical Society: Pennington, NJ, 1995.
7. Steck, A. E.; Stone, C. In Proceedings of the 2nd International Symposium on New Materials for Fuel Cells and Battery Systems; Montreal, Canada, 1997.
8. Rafler, G.; Ulrich, H.; Bauer, B. In Polymerwerkstoffe'96, Merseberg, September 18–20, 1996.
9. Wnek, G. E.; Rider, J. N.; Serpico, J. M.; Einset, A. G.; Ehrenberg, S. G.; Tangredi, T. N.; Robin, L. In Proton Conducting Membranes for Fuel Cells I, PV 95-23, The Electrochemical Society Proceedings Series; Gottesfeld, S., Halpert, G., Landgrebe, A., Eds.; Electrochemical Society: Pennington, NJ, 1995.
10. Chapiro, A. Radiation Chemistry of Polymeric Systems; Wiley–Interscience: New York, 1962.
11. Gupta, B.; Scherer, G. G. Chimia 1994, 48, 127.
12. Büchi, F. N.; Gupta, B.; Rouilly, M.; Hauser, C.; Chapiro, A.; Scherer, G. G. In Intersociety Energy Conversion Engineering Conference; San Diego, CA, August 3–7, 1992.
13. Gupta, B.; Büchi, F. N.; Scherer, G. G. Solid State Ionics 1993, 61, 213.
14. Büchi, F. N.; Gupta, B.; Scherer, G. G. Electrochim Acta 1995, 40, 345.
15. Guzman-Garcia, A. G.; Pintauro, P. N.; Verbrugge, M. W.; Schneider, E. W. J Appl Electrochem 1992, 22, 204.
16. Wang, H.; Capuano, G. A. J Electrochem Soc 1998, 145, 780.
17. Sugiyama, S.; Tsuneda, S.; Saito, K.; Furusaki, S.; Sugo, T.; Makkuchi, K. React Polym 1993, 21, 187.
18. Zhli-Li, X.; Gen-Hu, W.; Han-Ing, W.; Gyn, C.; Min-Hua, N. Radiat Phys Chem 1983, 22, 939.
19. Holmberg, S.; Lehtinen, T.; Näsman, J.; Ostrovskii, D.; Paronen, M.; Serimaa, R.; Sundholm, F.; Sundholm, G.; Torell, L.; Torkkeli, M. J Mater Chem 1996, 6, 1309.
20. Holmberg, S.; Näsman, J.; Sundholm, F. Polym Adv Technol 1998, 9, 121.
21. Brack, H. P.; Büchi, F. N.; Rota, M.; Scherer, G. G. Polym Sci Eng 1998, 77, 368.
22. Nasef, M. M.; Saidi, H.; Nor, H. M.; Dahlan, K. M.; Hashim, K. J Appl Polym Sci 1999, 73, 2095.
23. Nasef, M. M.; Saidi, H.; Nor, H. M.; Ooi, F. M. J Appl Polym Sci 2000, 76, 1.
24. Rouilly, M. V.; Kötz, E. R.; Haas, O.; Scherer, G. G.; Chapiro, A. J Membr Sci 1993, 81, 89.
25. Nasef, M. M.; Saidi, H.; Nor, H. M. J Appl Polym Sci 2000, 76, 220.
26. Gupta, B.; Büchi, F. N.; Scherer, G. G. J Polym Sci Part A Polym Chem 1994, 32, 1931.
27. Hietala, S.; Holmberg, S.; Näsman, J.; Ostroviskii, D.; Paronen, M.; Serimaa, R.; Sundholm, F.; Torell,

L.; Torkkeli, M. Angew Makromol Chim 1997, 253, 151.
28. Gupta, B.; Büchi, F. N.; Scherer, G. G. Polym Adv Technol 1994, 5, 493.
29. Zawodzinski, T.; Davey, J.; Valerio, J.; Gottesfeld, S. Electrochim Acta 1995, 40, 297.
30. Halim, J.; Büchi, F. N.; Haas, O.; Stamm, M.; Scherer, G. G. Electrochim Acta 1994, 39, 1303.
31. Zawodzinski, T.; Derouin, C.; Radzinski, S.; Sherman, R. J.; Smith, V. T.; Springer, T. E.; Gottesfeld, S. Electrochem Soc 1993, 140, 1041.
32. Rieke, P. C.; Vanderborgh, N. E. J Membr Sci 1987, 32, 313.
33. Gupta, B.; Haas, O.; Scherer, G. G. J Appl Sci 1994, 54, 469.
34. Hietala, S.; Holmberg, S.; Karjalainen, M.; Näsman, J.; Paronen, M.; Serimaa, R.; Sundholm, F.; Vahvaselka, S. J Mater Chem 1997, 5, 721.
35. Gupta, B.; Scherer, G. G. J Appl Sci 1993, 50, 2129.
36. Hietala, S.; Keol, M.; Elomaa, M.; Sundholm, F. J Mater Chem 1998, 8, 1127.
37. Nasef, M. M.; Saidi, H.; Nor, H. M. J Appl Polym Sci 2000, 77, 1877.
38. Zawodzinski, T.; Näsman, J.; Sillerud, L.; Gottesfeld, S. J Phys Chem 1991, 95, 6040.
39. Nasef, M. M.; Saidi, H.; Nor, H. M. J Appl Polym Sci, to appear.
40. Du Pont. Product Technical Information, Nafion® Global Customer Service; Du Pont: Fayetteville, NC, 1993.